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Ethanol as the acyl acceptor for biodiesel production

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ABSTRACT

Biodiesel has potential as a substitute for petroleum diesel because of the increasing worldwide concern for environmental sustainability and dwindling petroleum resources. Methanol has been the commonly used alcohol for biodiesel production. Compared with methanol, ethanol can be derived from sugar- and starch-based feedstocks and lignocellulosic biomass. Therefore, using ethanol as the acyl acceptor for biodiesel (fatty acid ethyl esters, FAEEs) production is drawing increasing interest in recent years. There are extensive studies using various approaches for the preparation of FAEEs and the properties of these fuels have also been explored. This paper reviews the state-of-the-art technologies for FAEE preparation. At the end, the fuel properties of FAEEs as well as the limitations and perspectives of biodiesel production with ethanol as the acyl acceptor are highlighted.

Contents

1. Introduction

Fossil diesel runs a major part of the transport sector and also plays an important role in the world economy. Due to dwindling reserve of crude oil and augmented greenhouse gas emissions associated with over-consumption of petroleum-based products, particularly transportation fuels, alternative renewable fuels are

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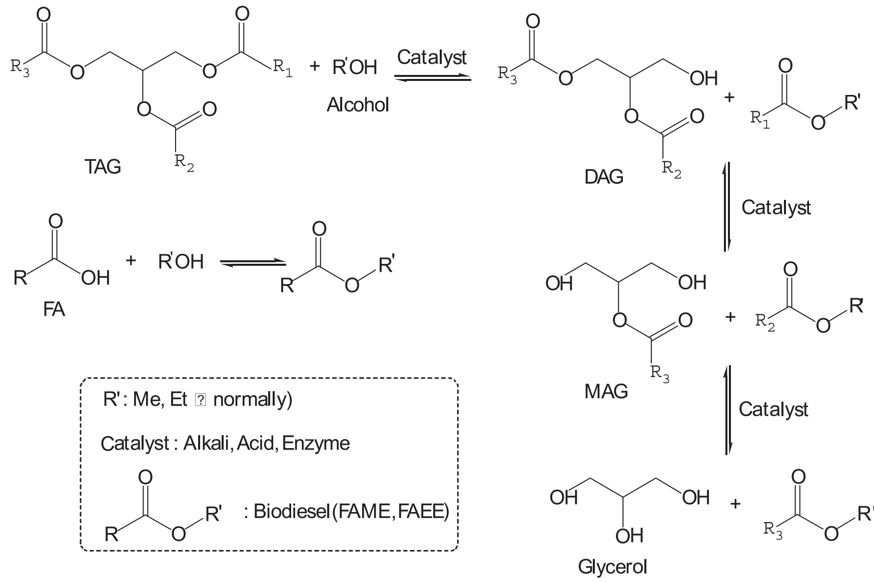


Fig. 1. Biodiesel production from renewable oils.

drawing tremendous attention in recent years [1]. Biodiesel, which is derived from triglycerides or free fatty acids by transesterification or esterification with short chain alcohols (Fig. 1), has attracted considerable attention in the past decade as a renewable, biodegradable, and nontoxic fuel [2,3].

Currently, industrial-scale synthesis of biodiesel is generally performed by the transesterification of renewable oils with methanol as the acyl acceptor. However, exploring ethanol as the acyl acceptor for biodiesel production is drawing increasing attention mainly due to the advantages of ethanol of being less toxic than methanol and it can be derived from renewable resources, thereby attaining total independence from petroleum-based alcohols [4–7]. Another attractive properties of biodiesel produced from ethanol are that FAEEs have higher heat content and cetane number compared to methyl esters (FAMEs) due to the extra carbon contained in ethanol [4,8,9].

There have been extensive studies related to using various approaches such as homogeneous alkali/acid catalysis, heterogeneous alkali/acid catalysis, enzyme catalysis, and catalysis in supercritical fluid system for the preparation of FAEEs. Meanwhile, comparison studies have been done on the properties of biodiesel with methanol and ethanol as the acyl acceptor. This paper reviews the state-of-the-art technologies for FAEEs' preparation, and highlights their related fuel properties. Finally, the constraints and perspectives of biodiesel production with ethanol as the acyl acceptor are also discussed.

2. Ethyl ester production with various approaches

2.1. Homogeneous catalysis

2.1.1. Alkali-mediated catalysis

Homogeneous alkali-mediated catalysis is the most widely used method in biodiesel production, especially with refined plant oils as the feedstocks. Normally, alkali catalysts include hydroxides and alkoxides of alkali metals, such as KOH, NaOH, CH_3ONa, CH_3OK, and so on. These catalysts have been explored not only as the catalysts for methyl ester production, but also for the ethyl ester preparation [4,6,10,11].

It has been demonstrated that the variables influencing the ethanolysis reaction are similar to those influencing the methanolysis reaction, including the type as well as the amount of the catalyst, the molar ratio of alcohol to oil, the reaction temperature, the agitation intensity and the quality of feedstocks (Table 1).

Table 1
Homogeneous alkaline catalyst-mediated ethanolysis.

Catalyst	Temperature (°C)	Ethanol to oil molar ratio	Catalyst wt%(oil)	Reaction time (h)	FAEE yield (%)	Reference
NaOH	30	7.5:1	0.675	2.5	99.5	[1]
NaOH	38	11.7:1	0.6	6	99.1	[12]
NaOH	60	12:1	1	2	66.2	[9]
KOH	90	11:1	1.75	1.5	86.3	[10]
KOH	35	6:1	1.5	1	98.0	[13]
KOH	60	12:1	1	2	72.5	[9]
$NaOCH_3$	60	12:1	1	2	59.4	[9]
$KOCH_3$	60	12:1	1	2	63.9	[9]

Compared to methanolysis, the reaction rate of ethanolysis is slower to certain extent [10,12,13]. It was reported that using ultrasonic irradiation and microwave could fasten the reaction rate during the ethanolysis process. Hanh et al. found that the ultrasonic field induced an effective emulsification and the rate of the ester formation under the ultrasonic irradiation was higher than that in the stirring condition [14]. Kumar et al. reported that using the ultrasonic mixing method enabled shorter reaction time and less energy consumption compared to the conventional mechanical stirring approaches [15]. Suppalakpanya et al. and Kanitkar et al. developed a homogeneous alkali-mediated transesterification process with a microwave heating system to facilitate the ethyl ester production, offering major advantages of considerable reduction in catalyst amount (~10-fold) and higher reaction rates (up to 10 times faster) [16,17].

Another major difference between methanolysis and ethanolysis with homogeneous alkali as the catalyst is that during the ethanolysis process, the emulsion of the system is more serious resulting in more difficult in product separation and downstream processing [9,18]. Short chain alcohols, including methanol and ethanol are not miscible with triglycerides at room temperature, and the reaction mixture is usually mechanically stirred to enhance the mass transfer. During the reaction process, emulsions

are usually formed. It has been found that in the case of methanolysis, the emulsion broke down easily by stopping the mechanical stirring after the reaction completion, resulting in the formation of a glycerol rich layer and a methyl ester rich layer. However, in the process of ethanolysis, the emulsion is more stable compared to that formed in the methanolysis, making the separation and purification of FAEEs more complicated [19]. Further studies need to be carried out by taking the downstream separation into consideration when homogeneous alkali is adopted as the catalyst for FAEEs' production.

2.1.2. Acid-mediated catalysis

Although the transesterification reaction catalyzed by acid is considerably slower than that catalyzed by alkali, the acid catalysts are still drawing much attention due to their advantages of being capable of simultaneously catalyzing both esterification and transesterification of oil feedstocks for biodiesel production [20].

Just like homogeneous acid-mediated reaction in FAMEs' production, surphuric acid is also the most widely used catalyst in FAEEs preparation. The reactions are found to be influenced by molar ratio of ethanol to oil, reaction temperature, concentrations of catalyst, and reaction time [16,17,21]. For instance, it was found that increasing the molar ratio of ethanol to oil from 4.5 to 9.0, the conversion increased from 75% to 90% [22]. Reaction rate of acid-catalyzed reaction may also be influenced significantly by the amount of catalysts. Typically, the amount of catalyst ranging from 0.5 wt% to 5 wt % is adopted in most studies, especially with sulfuric acid as the catalyst [23,24].

Apart from the above factors influencing homogeneous acid-mediated reaction, pronounced negative effects of water on the reaction were also observed [25,26]. Aafaqi et al. showed that when reaction was carried out with 15 vol% water initially present in the system, the conversion decreased by around 40% [25]. Hu et al. found that the acid catalyst lost about 30% of its catalytic activity when 7.5 mol% water was introduced into the esterification system [26].

2.2. Heterogeneous solid catalysis

Heterogeneous solid catalysts are extensively studied especially during the process with methanol as the acyl acceptor for biodiesel production. Compared to homogeneous catalysts, the major advantages of using heterogeneous solid catalysts are their properties of being recyclable as well as being easy for purification of the products. In recent years, heterogeneous solid catalyst-mediated biodiesel production with ethanol as the acyl acceptor has also been explored [27–30].

2.2.1. Solid alkali-mediated catalysis

The homogeneous alkali-mediated catalysis has several disadvantages including non-recoverability of the catalyst for its reuse, generation of waste water (in the washing step) and salt by-products (in the neutralization step). To overcome these disadvantages, heterogeneous solid alkali catalysts have been proposed and the related studies with ethanol as the acyl acceptor for FAEEs production are summarized in Table 2.

Generally, the type of solid alkali catalyst, the temperature, the molar ratio of ethanol to oil as well as the amount of catalyst are demonstrated to have varied influence on the ethanolysis reaction [29–31]. Compared with methanolysis, the yield as well as the reaction rate of ethanolysis was found to be much lower [28,31]. For instance, $Zn_5(OH)_8(NO_3)_2$-mediated methanolysis and ethanolysis were studied for comparison, and the yields of methyl ester and ethyl ester were found to be 87.1% and 77.2% respectively [31]. The same phenomenon was also observed by other researchers, which was attributed to the greater steric hindrance effect of ethanol compared to methanol as the acyl acceptor for biodiesel production [32,35].

2.2.2. Solid acid related catalysis

Solid acid related catalysts are Lewis acids and their catalysis activities depend not only on the strength of acid but also the characteristics of the solid surface [36]. In recent years, solid acid-mediated reaction with ethanol as the acyl acceptor for biodiesel production has also been explored and the related researches are summarized in Table 3.

As can be seen from Table 3, the type of solid acid catalyst, the temperature, the molar ratio of ethanol to oil as well as the amount of catalyst have significant influence on the solid acid-mediated reaction in FAEEs' production [36,38,39]. Some double-metal cyanide (DMC) solid acid catalysts were developed and showed good performance in the production of FAEEs from a variety of low-grade oils [37]. These DMC catalysts are acidic, hydrophobic and insoluble in most of solvents and the performance of these solid catalysts in catalyzing FAEEs' production is just a little worse than that in catalyzing FAMEs' preparation.

Various ion-exchange resin catalysts have also been explored as the solid acid catalysts for FAEEs' production. It was found that the anion-exchange resins exhibited much higher catalytic activities than the cation-exchange resins, which was thought to be due to the characteristics of lower cross-linking density and smaller particle sizes of the anion-exchange resins [38].

Although solid acid catalysts have the capability of catalyzing both esterification and transesterification of oil feedstocks for

Table 2
Solid alkali-catalyzed reaction with ethanol as the acyl acceptor.

Catalyst	Temperature (°C)	Ethanol to oil molar ratio	Catalyst wt%	FAEE yield %	Reference
$Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$	140	6:1	2	77.2	[31]
Dowex monosphere 550A	30–55	4:1–6:1	2.2	70–95	[29]
Dowex monosphere 550A	55	6.13:1	3	~15	[32]
Dowex monosphere 550 A	45	6.13:1	1.75	75	[33]
Dowex upcore mono A-625	45	6.13:1	2.2	20	[33]
Dowex marathon A	54	10:1	3	29.5	[28]
Modified zirconia	40	5:1	10	25	[30]
MgCoAl–LDH	100	16:1	2	96–97	[34]
$CaO–La_2O_3$	65	10:1	–	71.6	[28]

Table 3
Solid acid-catalyzed reaction with ethanol as the acyl acceptor.

Catalyst	Temperature (°C)	Ethanol to oil molar ratio	Catalyst amount wt% (oil)	FAEE yield (%)	Reference
Amberlyst-26	45	6:1	3	63	[35]
Double-metal cyanide	170	15:1	3	> 90	[37]
Anionic ion-exchange resin	50	20:1	20	~85	[38]
$H_3PW_{12}O_{40}$	80	6:1	0.6	95	[39]
Sulfated zirconia	120	12:1	10	45	[36]

biodiesel production, the reaction rate of the transesterification is much slower than that of the esterification [38]. So far, there are few studies regarding the comparison of solid acid-mediated FAEEs' and FAMEs' production, especially on the reaction rate and the final biodiesel yield.

2.3. Enzymatic catalysis

Enzymatic approaches for biodiesel production have also received much attention in recent years, since they have many advantages over chemical methods: moderate reaction conditions, low alcohol to oil ratio, easy product recovery and environmental friendliness. Besides, free fatty acids (FFAs) contained in low-grade oils can be completely converted to alkyl esters in the same process [2]. Lipase from *Pseudomonas flseudomona, Pseudomonas cepacia, Candida rugosa, Candida Antarctica, Rizhomucor miehei*, and *Thermomyces lanuginosa* are the most extensively studied lipases both in conventional conditions and in supercritical fluid for FAEEs' production [40–44].

2.3.1. Enzyme catalysis in conventional conditions

In terms of the forms of biocatalyst, the enzyme-mediated biodiesel production can be classified into immobilized lipase, whole cell catalyst, and liquid lipase-mediated alcoholysis. At present, immobilized lipases are studied most widely as the catalysts for FAEEs' production and the related studies are summarized in Table 4.

Solvent-free system was first proposed for lipase-mediated methanolysis for biodiesel production [42,48,49]. Like enzyme-mediated FAMEs' production, the molar ratio of ethanol to oil also showed significant influence on lipase's catalytic performance in FAEEs' preparation. Stepwise addition of ethanol or introducing organic solvent into the reaction system was found to be beneficial to maintaining the enzymes' catalytic performance [42,47].

Watanabe et al. studied stepwise addition of ethanol and the conversion could reach up to 95% [47]. Rodrigues et al. also found that two-step ethanolysis was very effective to avoid the negative effect caused by ethanol and a conversion rate of around 100% could be obtained [42]. Du et al. proposed introducing a hydrophilic solvent tert-butanol as the reaction medium for FAMEs' production and the operational stability of the lipase was improved significantly [2,50]. It was also found that using tert-butanol as the reaction medium was favorable for maintaining the high catalytic activity of the lipase in enzyme-mediated ethanolysis for FAEEs' production [40].

Apart from immobilized lipase, whole cell producing intracellular lipase as well as liquid lipase has also been explored for FAEEs' production in recent years. Utilizing whole cells instead of conventional immobilized lipase as the catalyst for biodiesel production is a potential way to reduce the cost of biocatalyst, since they can avoid the complex procedures of lipase fermentation, purification and immobilization. *Rhizopus oryzae*, a species producing intercellular lipase, has been studied extensively for biodiesel production, and it has been demonstrated that the immobilization of such whole cells can be realized spontaneously during the process of cell cultivation [51,52]. It was reported that lipase-producing fungal cells immobilized on BSPs could catalyze the ethanolysis of rapeseed oil and the yield of FAEEs could reach 94% [53].

Liquid lipase offers an alternative approach to enzyme-catalyzed biodiesel production. Compared with immobilized lipase, liquid lipase has the advantages of faster reaction rate and lower cost; and hence much attention has been paid to liquid lipase-mediated methanolysis for biodiesel preparation in recent years [41,54]. It was found that liquid lipase was capable of catalyzing the ethanolysis of triglycerides to produce biodiesel in an oil/water biphasic system and the biodiesel yield of over 90% could be obtained [41]. Although the recovery of lipase and the enzyme's performance during continuous running need to be further evaluated, liquid lipase-mediated ethanolysis provides an alternative way for FAEEs' production.

Table 4
Immobilized lipase-mediated FAEEs' production.

Lipase sources	Ethanol to oil molar ratio	Catalyst amount wt% (oil)	Reaction time (h)	FAEE yield (%)	Reference
Pseudomonas cepacia	15.2:1	4.75	1	65	[46]
Candida antarctica	1:1	4	10	32.9	[47]
Candida antarctica	4:1	5	24	88.9	[40]
Thermomyces lanuginosus	9:1	15	10	~100	[42]
Mixed lipases	4:1	10	12	~85	[43]

2.3.2. Enzyme-mediated FAEEs' production in supercritical fluid system

Compared to conventional media, supercritical fluid has the characteristics of its density being close to the liquid, while the viscosity close to the gas, and thermal conductivity and diffusion coefficient between gas and liquid, giving improved solubility of oil and alcohol and accelerated transesterification reaction.

Carbon dioxide and propane have been proposed as the compressed fluids for enzyme-mediated ethanolysis [55]. It was reported that in a continuous process of Novozyme 435-mediated FAEEs' production in compressed carbon dioxide, the yield of FAEE could reach up to 90% with the reaction carried out at 70 °C, 150 bar, oil to ethanol molar ratio of 1:20, and solvent to substrates mass ratio of 4:1 [56]. In the compressed propane, lipase-catalyzed ethanolysis was also explored, where the conversion of 90% could be obtained with immobilized lipase Novozym 435 as the catalyst [55–57].

Generally speaking, the compressed fluids are associated with high cost in compressing gas to liquid and more studies need to be carried out especially in terms of the possibility of further practical application.

2.4. Catalyst-free reaction in supercritical fluid alcohols

Short chain alcohols such as methanol and ethanol are hydrophobic in supercritical conditions, and triglyceride dissolves well in them. As a result, biodiesel production in the supercritical system has advantages of quick reaction rate and high converting yield [45,58]. It was reported that biodiesel could be produced at a relatively fast rate without the presence of catalyst by heating up alcohol (either methanol or ethanol) to its supercritical stage [59].

In supercritical fluid alcohols, FAEEs production was found to be influenced by temperature, pressure and molar ratio of ethanol to oil. The related studies were summarized in Table 5. In order to

Table 5
FAEEs production in catalyst-free supercritical fluid alcohols.

Temperature (°C)	Pressure (bar)	Ethanol to oil molar ratio	Residence time (min)	FAEE yield (%)	Reference
349	150–250	33:1	29	79.2	[45]
300	200	20:1	40	40	[60]
300	200	40:3	–	97.3	[58]
350	200	40:1	–	~60	[61]
225	200	20:1	–	59.9	[62]

reach the supercritical state, the reaction usually needs to be conducted at the conditions of temperature of above 200°, pressure of above 150 bar and molar ratio of ethanol to oil greater than 20:1 [45,60,63,64].

It is worth mentioning that the effect of molar ratio of ethanol to oil is not consistent in the literature. Some studies showed that the increase in molar ratio of ethanol to oil benefited the ethanolysis, while other studies demonstrated negative effect caused by increase of the molar ratio of ethanol to oil [62,65]. To reduce the operating cost and product degradation, co-solvent carbon dioxide was introduced for FAEEs production in supercritical ethanol and the yield of FAEEs was found to increase with the increase of co-solvent addition [65]. More studies need to be carried out to evaluate its practical application.

3. Properties and engine performance of FAEEs

3.1. Physico-chemical properties of ethyl ester vs. methyl ester

The comparison study on the properties of FAMEs and FAEEs produced from various oil feedstocks has been conducted and the related results are summarized in Table 6.

Through Table 6, it can be noticed that FAEEs and FAMEs share the similar properties in most aspects as an alternative fuel to traditional fossil fuel. The oxidation stability of FAEEs is even higher than that of FAMEs. Besides, the cloud point of FAEEs is much lower than that of FAMEs, indicating the flow properties of FAEEs at cold temperature are much better than that of FAMEs. The flash point of FAEEs is also slightly higher than that of FAMEs, which means the FAEEs fuel has a better safety and ignition performance. Since FAEEs have one more carbon compared to FAMEs, the calorific value of FAEEs is also slightly higher than that of FAMEs.

The study on the properties of FAEEs produced from sunflower oil and Brassica carinata oil has also been carried out, giving the similar results as elaborated in Table 6.

3.2. Engine performance of FAEEs

At present, the study on engine performance of FAEEs is mainly focused on the emissions and power performance. It is found that compared to fossil diesel, there is an obvious reduction in the emissions by using FAEEs as the vehicle fuel, such as HC decreased by 55.6%, CO decreased by 50.6% and NO decreased by 11.8% [69]. Based on various blending of FAEEs in fossil diesel, the emissions for the arterial cycle, which consist of eight replications of accelerating to 64.4 km/h (40 mile/h) and decelerating to 0 km/h (0 mile/h), and EPA cycle (the dynamometer driving schedule for heavy duty vehicles) have been conducted and the related results are shown in Table 7 [69]. The result shows that with increase of the blending ratio of FAEEs in fossil diesel, the emissions of HC, CO and CO_2 decrease obviously in both Arterial cycle and EPA cycle. B20 gives the lowest emission in either Arterial cycle or EPA cycle, while there is almost no significant reduction in CO_2 emission in both cases.

Further, the dynamometer test result of FAEEs as engine fuels indicates that there is no noticeable difference in engine power

Table 6
Properties of FAEES and FAMEs.

Property	Karanja oil		*Camelina sativa* oil		Soybean oil		Rice bran oil		Soybean oil	
	FAMEs	FAEEs	FAMEs	FAEEs	FAMEs	FAEEs	FAMEs	FAEEs	FAMEs	FAEEs
Density, @15 °C, g/cm^3	0.88	0.88	–	–	–	–	–	–	–	–
Viscosity, @40 °C, cst	3.99	4.57	4.15	4.48	4.12	4.41	5.54	5.09	4.12	4.60
Flash point, °C	160	178	–	–	–	–	153.5	156.5	–	–
Iodine value, gI2/100g	86.5	86.5	151	144	134	127	–	–	136	130
Oxidative stability, h	–	–	2.5	2.9	5.0	6.0	6.87	7.79	5	6.5
Cloud point, °C	12	10	3	2	0	0	5.35	5.10	2	0
Pour point, °C	5	4	−4	−4	−3	−4	–	–	0	−2
Reference	[66]		[67]				[68]		[5]	

Table 7
Emissions test for various blending of FAEEs and fossil diesel.

Emission contents	Arterial cycle				EPA cycle			
	diesel	B20	B50	B100	Diesel	B20	B50	B100
HC	0.833	0.668	0.541	0.332	1.25	1.021	0.834	0.592
CO	3.28	2.38	1.84	1.74	4.50	2.92	2.23	2.11
NO_x	6.23	5.98	5.72	5.53	6.85	6.44	6.31	6.01
CO_2	651.7	653.4	657.5	658.1	698.6	708.2	698.3	707.0
PM	0.301	0.286	0.337	0.305	0.411	0.386	0.428	0.480

Table 8
Results of the dynamometer tests of the biodiesel fueled pickup.

	2253 km beginning		12100 km middle		25554 km end	
	Diesel	B100	Diesel	B100	Diesel	B100
Power @2500 rpm (kW)	108	108	108	105	109	106
Fuel efficiency @2500 rpm (g/MJ)	79.6	86	80.9	87.9	78.6	86.3
Percent opacity snap idle test (% opacity)	21.5	18.4	26.1	15.5	27	17

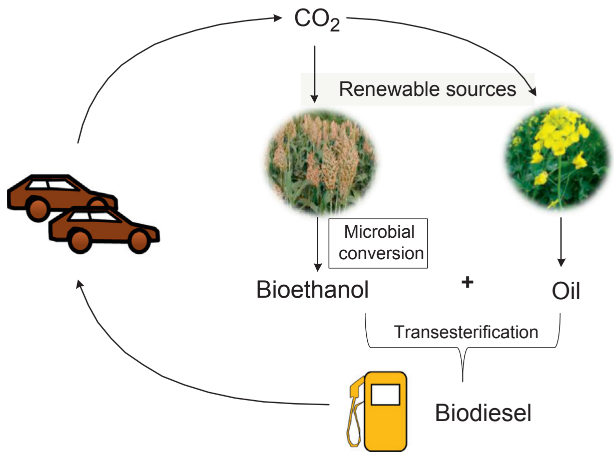


Fig. 2. Concept description of using bioethanol for biodiesel preparation.

Triglyceride + 3 Ethanol ⟶ 3 Ethyl ester + Glycerin

881 g/mol   138 g/mol   927 g/mol   92 g/mol

Fig. 3. FAEEs production from triglycerides and ethanol.

between fossil diesel and B100, but fuel efficiency of B100 is much higher than that of fossil diesel in the tests (Table 8) [69].

The engine performance study on various blending ratio of FAEEs in fossil diesel (B5, B10, B15, B20, B25 and B30) has also been carried out [70]. It was found that average reductions of 1.16%, 1.73%, 0.55% and 0.36% were observed in the specific fuel consumption for B5, B10, B15 and B20 blends, respectively, while increases of 0.52% and 1.18% were observed respectively, for B25 and B30 blends.

4. Prospects and impacts of using bioethanol for biodiesel production

Depletion of fossil fuel deposits, threat of supply instability, rising petroleum prices, and increasing threat to the environment from exhaust emissions cause the reactivation of worldwide interest in renewable biofuels. Although currently all commercial biodiesel is produced from plant oils and methanol as the source of alcohol, the depleting fossil sources have caused uncertainty to the supply and cost of products derived from fossil sources, including methanol. In contrast, ethanol can be easily produced from biomass that can be found abundantly via fermentation process and this type of ethanol is commonly known as bioethanol. There is already commercial production of bioethanol as a substitute fuel for gasoline, and the supply of bioethanol for the production of biodiesel seems promising. Therefore, with the utilization of bioethanol as the source of alcohol, the biodiesel obtained can then be claimed as 100% renewable based (Fig. 2).

Since the molecular structure of ethanol and methanol only differs by one methyl group, there is not much difference between the chemical and physical properties of FAMEs and FAEEs fuels. Studies even indicate that FAEEs presents the following advantages over commonly used FAMEs [19]: lower particulate matter and green-house emissions, more biodegradable in water, higher cetane index and heating power, and lower cloud point, cold filter plugging and pour points, which makes FAEEs more attractive as an alternative fuel to traditional fossil fuel. Besides, from an economical point of view, there is another important advantage of FAEEs over FAMEs as the alternative fuels, which is related to the reaction stoichiometry as shown in Fig. 3. When the process yield is defined as the FAEEs/triglyceride mass ratio, the maximum yield is 105.2% (ton of biodiesel/ton of oil) for ethanol, as compared to 100.5% for methanol.

To sum up, although ethanol has lower transesterification reactivity in comparison with methanol caused by steric hindrance of longer carbon chain and ethanol is currently more expensive than methanol, the environmental advantages of FAEEs, as well as the potential economical benefits, make FAEEs promising as an alternative fuel to fossil diesel.

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